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Studies on the effects of γ-radiation on the mechanical properties of Nylon 6–12 fibers

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SUMMARY

Commercial nylon 6-12 fibers were subjeted to various doses of γ-radiation. The mechanical and some thermal properties,as compared to those of non-irradiated fibers, show changes which are discussed in terms of the radiation-matter interactions.

INTRODUCTION

Nylon is one of the most cost-effective engineering thermoplastics available. Part of the reason for this characteristic is the versatility of polyamides for modification and reinforcement, for more than 300 variants of nylon have been reported(1). The high degree of crystallinity of these polyamides provides high melting points, of practical relevance for many applications. Also, the high mechanical strength of cristalline nylon fibers renders them attractive for fishing nets and as reinforcing elements in polymer-polymer composites.

It is known that control of the crystallization of nylons results in some degree of control of the corresponding mechanical properties. Since different kinds of ionizing radiation have proven effective in controlling amorphization of many materials, ranging from polymers (2-5) to minerals (6), in recent years, the interest in studying radiation-polymer interactions has been renewed. In addition to the technological interest in controlling crystallinity, there exist some fundamental questions on the details of the structural changes that nylons undergo when subjected to external energy sources (7-12). Specifically, some nylons show the so-called Brill transition (10,11) when heated and little is known about similar transitions with other types of excitations.

In this work, the changes in mechanical properties of 6-12 nylon fibers when subjected to γ-radiation, are reported.

EXPERIMENTAL

a) Materials

Nylon 6-12 fibers, were obtained from Dupont (Zytel) in two forms: amorphous and crystalline. The amorphous fibers have a diameter of 0.425mm. and the crystalline ones of 0.2mm."Amorphous" in this work means a negligible degree of crystallinity, whereas "crystalline" exhibits the highest cristallinity achievable.

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b) Irradiation procedure

The material were subjected to gamma-irradiation in dosages from 10-400 KGy at room temperature. The dose rate was 2.3 KGy/h . The irradiation was provided by a JS6500 gamma irradiator from Atomic Energy of Canada Limited (AECL now Nordion International INC), located at the Instituto Nacional de Investigaciones Nucleares (ININ). The dosimetry control of the irradiation process was carried out continuously using a red acrylic dosimeter L9C1(13).

c) Characterization techniques

Scanning electron microscopy of the fibers, before and after irradiation was performed on a JEOL-5200 microscope at 10 KV and in secondary electrons mode. The samples were glued with coloidal silver paint to the microscope holders and then a thin layer gold was evaporated onto the specimens to prevent electrostatic charging effects. X-Ray diffraction was carried out in a single-crystal setup in a Siemens D-500 diffractometer with Cu, Kα radiation at a scanning rate of 4 °/minute. Mechanical tensile testing was done in either an Adamel-Lhomargy Dy-22 or an Instron machines. The elongation and the strength at break were evaluated for fibers before and after irradiation. The melting temperature and the heat of fusion of the fibers were evaluated by a Dupont 2100 differential scanning calorimeter under N_2 atmosphere.

RESULTS AND DISCUSSION

Figure 1(a) shows the dependence of the melting temperature of the amorphous fibers as a function of the applied γ dose. The thermodynamic effect of irradiating the fibers can be further appreciated in Figure 1(b), where the corresponding heat of fusion is displayed. These two are important thermodynamic parameters which characterize the inter and intra-molecular events .

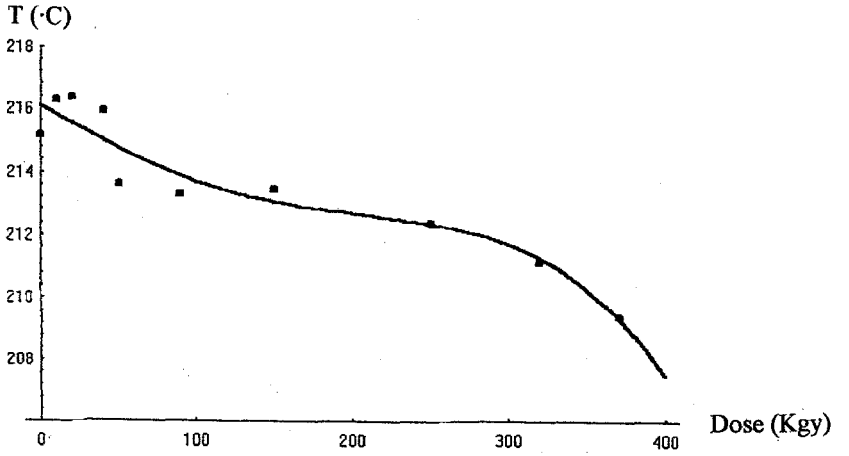


Fig. 1(a) Melting temperature of amorphous fibers vs. dose.

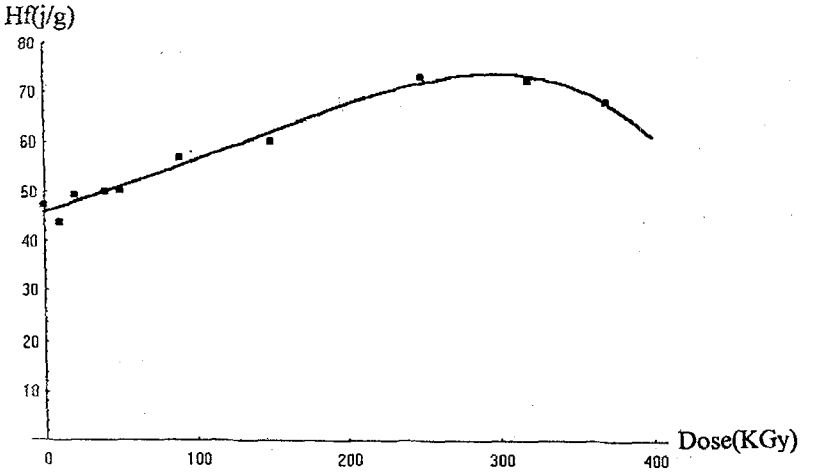


Fig 1(b) Heat of fusion of amorphous fibers vs. dose.

The melting temperature curve shows basically three regions. The first one, up to about 200 KGy corresponds to a steady decrease of the melting temperature of the polymer as the dose is increased. The second region up to 300kgy is essentially a plateau, where, the γ irradiation shows little effect on the melting temperature. The third region shows a very sharp decrease in melting temperature as the dose is increased. It is interesting to compare this curve with the change in the heat of fusion, where the first region corresponds to an increase of the heat of fusion, the second region is a maximum and the third region shows an abrupt decrease of heat of fusion when the dose increases. The empirical Nerst-Lindemann equation, as well as some more recent improvements [14-16] allow to relate the melting temperature to the corresponding heat capacity. Recent work [14] has shown that there exists an empirical numerical relation between the heat capacity of nylon and the number of methylene and amide groups in several nylons, including the 6-12. Qualitatively, the combination of the Nerst-Lindemann equation with the last empirical relation, indicates that the change in the relative number of methylene and amide groups in the chain can help to explain the observed behavior in the melting temperature as a function of dose. Indeed, some work on γ irradiation of 1010 crystalline nylon [2] indicates that the hydrogen bonds are more susceptible to radiation action. Also, according to Keller's model [17], the damage in semicrystalline polymers induced by γ-radiation spread from the surface inwards and, in the first stage of irradiation, the radiation-induced chemical reactions occurr solely in the non-crystalline regions. A second stage involves the decrease of microcrystal size with radiation dose, with an activation energy smaller than that of first stage. Finally, in the third stage, the chemical bonds within the crystallites are affected.

Figures 2(a) and 2(b) correspond to the change in maximum stress attained vs. dose and elongation at break vs. dose, respectively for amorphous fibers, whereas Figures 3(a) and 3(b) are the equivalent plots for the crystalline fibers.

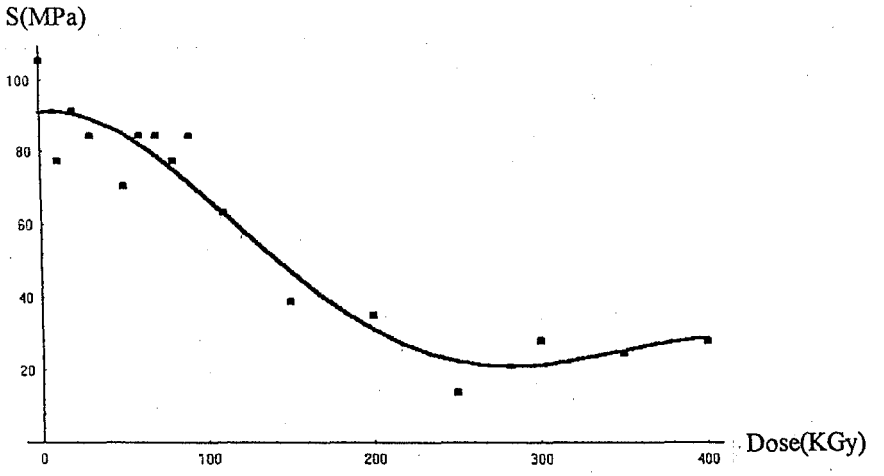


Fig.2(a) Maximum stress of amorphous fibers as a function of dose..

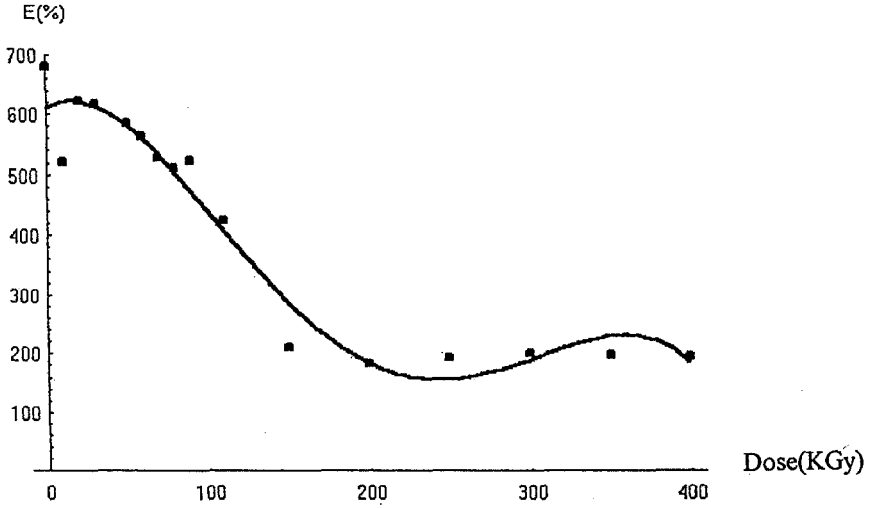


Fig. 2(b) Elongation at break of amorphous fibers as a function of dose

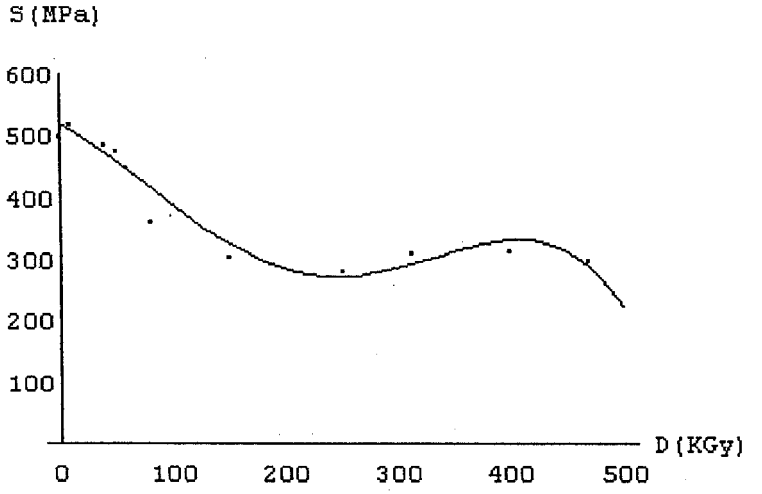


Fig. 3(a) Maximum stress of crystalline fibers as a function of dose.

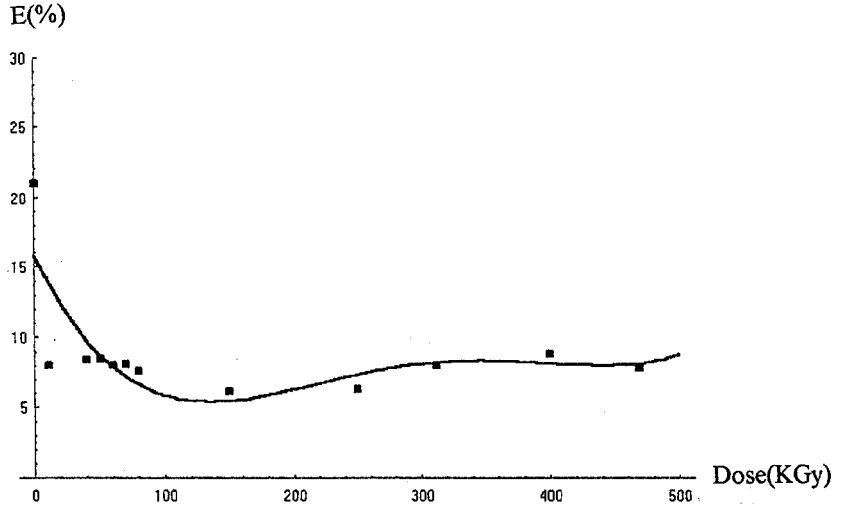


Fig. 3(b) Elongation at break of crystalline fibers as a function of dose

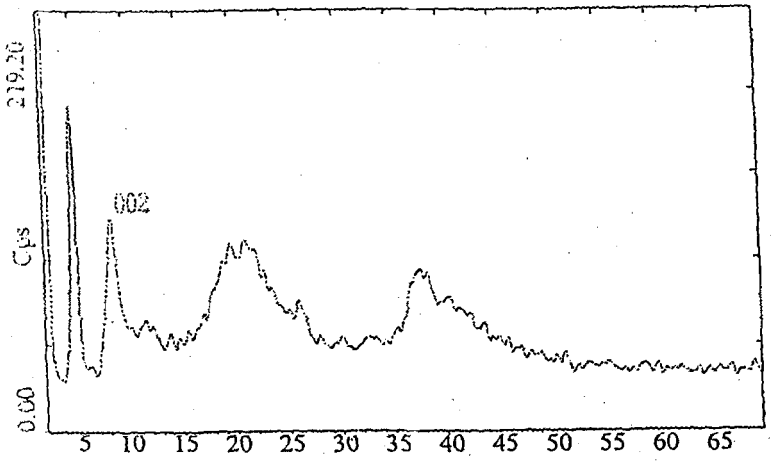


Fig. 4(a) X-ray diffractogram of crystalline fibers taken along the fiber axis.

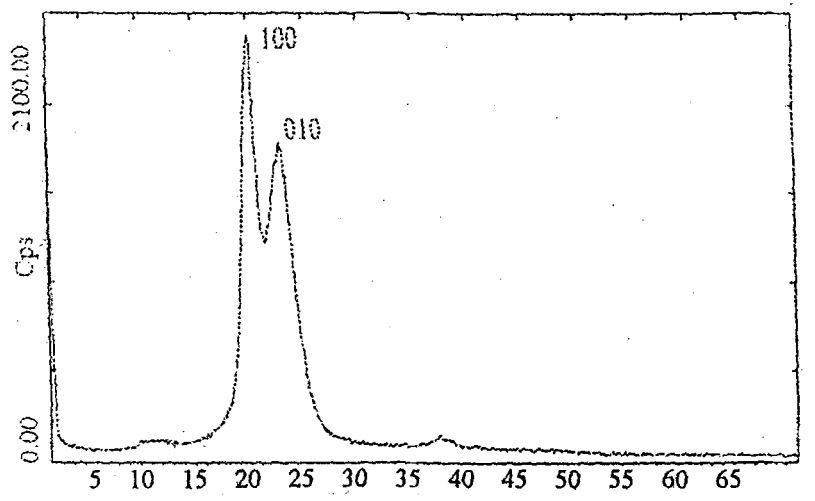
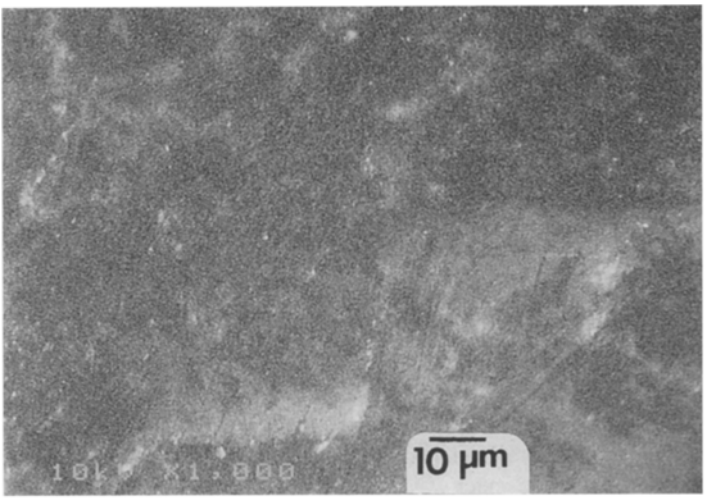


Fig. 4(b) X-ray diffractogram of crystalline fibers taken across the fiber axis.

(a)



(b)

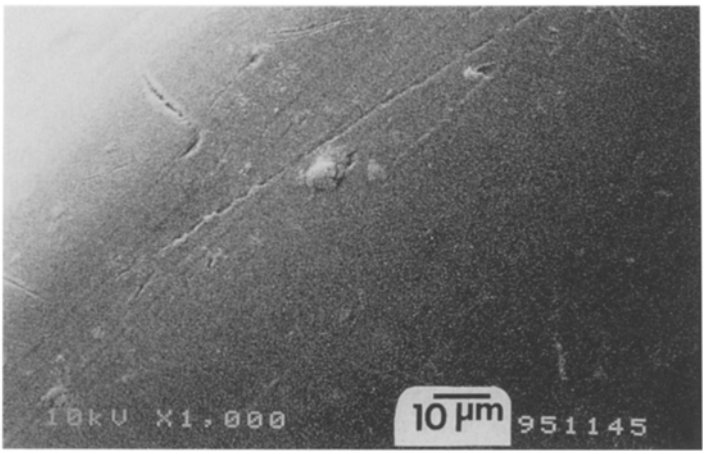


fig 5(a) SEM micrograph of amorphous fibers, after irradiated at 350 KGy.

fig 5(b) SEM micrograph of crystalline fibers, after irradiated at 350 KGy.

As can be observed , the effect of radiation on both types of fibers is detrimental. However, at higher doses an interesting plasticization is detected by which the elongation of the fibers begin to increase . It must be pointed out that the effect on the amorphous fibers is more severe than in the crystalline ones (450% vs. 170% relative decrease in maximum elongation). In fact, it has been reported (2) that the less-crystallized regions, with larger interfaces per unit volume of material, is damaged more easily by γ-radiation. On the other hand, it is also known that the effect of irradiation in crystalline nylon depends on the specific crystallographic plane (14-16). Figures 4(a) and 4(b) show the single crystal x-ray diffractograms of the crystalline fibers, prior to irradiation, along and across the fiber axis, respectively. The first case shows a peak identified as (002) and another reflection at low angle which could be attributed to the spatial arrangements of the crystallites. The diffractogram across the

fiber shows the typical (100) and (010) reflections. This indicates, first, the effect of the extrusion process on the spatial arrangement of crystallites and, second, the existence of the hydrogen bonds-containing (010) plane basically only across the fiber, for those peak, are poorly defined along the fiber. These planes are far more susceptible to damage when irradiated and also show a tendency to chain scission at higher doses, producing thus the observed effect on the mechanical properties. Figures 5(a) and 5(b) show SEM micrographs of amorphous and crystalline fibers after irradiation at 350 KGy, showing a much more marked effect on the amorphous fiber.

FINAL REMARKS

The results show that both the crystallinity and the anisotropy of the fiber clearly influence the degradation processes when subjected to γ-irradiation, as reflected in mechanical properties. A detailed analysis of the chemistry involved, by using FT-Raman spectroscopy is under way and will be reported separately.

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